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(54) Title: CHIRAL ADDITIVES FOR CHOLESTERIC DISPLAYS

(57) Abstract: A unique class of chiral additive materials is disclosed for use in cholesteric displays that possess a helical twist power substantially independent of temperature. The additives have a solubility and a helical twist power large enough to be used as a single chiral component with little dilution of the physical properties of the nematic liquid crystal host mixture. The chiral additives may be used in combination with non-chiral additives to provide a helical twisting power substantially independent of temperature suitable for cholesteric displays.

periodicity (pitch length) equal to the wavelength of light in the material. The first materials explored with this property were the cholesterol esters. These materials are not only chiral but also liquid crystalline and reflect iridescent colors when the periodicity of the twist corresponds to a reflective wavelength from 400nm to about 700nm ["Cholesteric Structure – II: Chemical Significance", p105 – 119, J. L. Fergason, N. N. Goldberg, R. J. Nadalin, *Liquid Crystals*, Ed. G. H. Brown, G. J. Dienes, M. M. Labes, Gordon and Breach Science Publishers, New York (1966)]. The materials were therefore called cholesteric liquid crystals, a name still used today even though cholesterol materials are seldom used today. Instead, a mixture of chiral and achiral compounds is used as discussed by Gottarelli *et al.* ["Induced Cholesteric Mesophases: Origin and Application, G. Gottarelli, G. P. Spada, *Mol. Cryst. Liq. Cryst.*, 123, 377 – 388 (1985)]. Achiral liquid crystalline compounds make up a nematic liquid crystalline host mixture, which has no helical twist by itself. To this host nematic is added a chiral compound to twist up the nematic material into one of a cholesteric structure, hence the name chiral nematic.

The helical arrangement of the molecules provides a self-assembled stack of dielectric layers because of the anisotropy of the refractive index of the molecules. The index of refraction continuously varies along the stack by as much as 0.25 depending upon the nematic material. Because of the helical nature of the refractive index in the layer, the stack will reflect one circular component of a selected bandwidth of colored light. A right handed twisted planar texture will therefore decompose incident unpolarized white light into its right and left components by reflecting the right hand component and transmitting the left. A left-handed twisted material will do the opposite. A left-hand display cell stacked on top of a right-hand cell, both with the same pitch length, will reflect all of the incident light.

According to Bragg's law, the wavelength λ , of the selective reflection is given by the equation: $\lambda = np$ where p is the pitch of the helical structure and n is the average refractive index of the liquid crystal mixture. In mixtures of a nematic liquid crystal with the chiral additive, the reciprocal of the pitch length is approximately proportional to the concentration X , of the chiral compound, $p^{-1} = \beta X$ with β being the helical twisting power (HTP).

Conventional chiral additives available today have twisting powers typically of $\beta < 15\mu\text{m}^{-1}$ when X is measured in weight percent.

Certain dimethanoldioxolane derivatives have been described in the literature as
5 possessing large HTP values. E.g., "TADDOLs with Unprecedented Helical Twisting Power
in Liquid Crystals", H. G. Kuball, B. Weiss, A. K. Beck, D. Seebach, *Helvetica Chimica
Acta*, 80, 2507-2514 (1997); "TADDOLs Under Closer Scrutiny – Why Bulky Substituents
Make it All Different", A. K. Beck, M. Dobbler, D. A. Plattner, *Helvetica Chimica Acta*, 80,
2073-2083 (1997); and in US Patent 5,637,255. Like other chiral additives, they are also
10 known to generally possess large temperature dependent values of dp/dT and, hence, $d\lambda/dT$.
Their temperature dependencies tend to be positive in that the pitch length increases with
increasing temperature, causing a cholesteric material to change from blue to red reflecting.
Furthermore, the temperature dependence dp/dT has been shown to depend on the material of
the host nematic. See "TADDOLs with Unprecedented Helical Twisting Power in Liquid
15 Crystals", H. G. Kuball, B. Weiss, A. K. Beck, D. Seebach, *Helvetica Chimica Acta*, 80,
2507-2514 (1997).

In order for flat-panel displays to be useful for portable applications, it is necessary
for the display be operable over a wide range of temperatures. Outdoor temperatures can
20 range from -20°C to $+50^{\circ}\text{C}$ depending on the environment. It would be advantageous if the
reflected colors did not change over this temperature range. Implementing this desirable
characteristic is not a straightforward task, since nearly all cholesteric liquid crystalline
materials are well known to exhibit reflective colors that vary strongly with changes in
temperature. Depending on the shape or chemical structure of the chiral molecule, the pitch
25 length p and, hence, the peak reflective wavelength λ , can increase with temperature
($+d\lambda/dT$) or decrease with temperature ($-d\lambda/dT$). Also, in many cases, $d\lambda/dT$ is not linear over
the temperature range of the cholesteric phase.

It should be mentioned at this point that the measurement for the temperature
30 dependence of the pitch is performed using test cells, each of which is $5\mu\text{m}$ thick, and has a
hard coat layer on both substrates. There is also an unrubbed polyimide surface on top of the

hard coat layers. The measurement for the temperature dependence of the pitch is performed in the following manner. A collimated light is incident on the display at surface normal and the reflected light is detected at 45°. The display is scanned in the wavelength band that includes the peak-reflected wavelength, e.g., 400nm to 700nm, or 700nm to 1500nm. The cell
5 is switched to the planar texture at each test temperature. The measurement is performed from -20°C to +70°C in 10°C intervals. It should be noted that, for the purposes of a flat temperature dependence, only a portion of the test temperature range, i.e., temperatures between +10°C to +50°C, are considered. In any event, the maximum change in peak reflected wavelength is then recorded. A mixture is considered to exhibit temperature
10 independent color behavior if the maximum change in the peak reflection wavelength is 30nm or less across the temperature range of +10°C to +50°C.

It has been shown that cholesteric displays fabricated using a mixture of two or more chiral compounds as additives can be made to produce a helical twist power and, hence,
15 reflective wavelength that is independent of temperature by combining a chiral compound that has a $+d\lambda/dT$ with one with a $-d\lambda/dT$. U.S. Patent No. 5,309,265 describes a means of achieving a temperature independent λ by combining a plurality of chiral compounds, where both compounds exhibit the same twist sense.

20 It will be noted that there are a number of factors that preclude employing many previously known chiral compounds in liquid crystals. First of all, a chiral compound must be soluble in the nematic liquid crystal host material; many compounds are simply not soluble or only weakly soluble and, thus, cannot be used. In compounds that are soluble, they may adversely affect the nematic material by substantially reducing the temperature range of the
25 liquid crystalline phase. If the chiral compound has an HTP that is too low, it may be necessary to add a large quantity of the additive which can dilute some of the desirable physical properties of the host nematic needed for the cholesteric display.

Consequently, a need still exists for a chiral additive, which is readily soluble in a
30 nematic host mixture and which can be used individually (i.e., without needing to be combined with other chiral materials) for cholesteric displays that provides a high helical

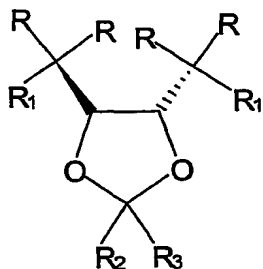
twisting power, substantially independent of temperature in operating ranges suitable for the cholesteric displays. What is also needed is a cholesteric display exhibiting a high helical twisting power, which is substantially independent of temperature in operating ranges suitable for the cholesteric displays, which display includes at least one chiral additive, which is readily soluble in a nematic host mixture. In some cases it would be desirable if the temperature dependence of the cholesteric display could be tailored by the addition of a second additive, e.g., either an achiral compound or a second chiral additive different from the first chiral additive, where the twist senses of the first and second chiral additives are opposite to one another.

SUMMARY OF THE INVENTION

The above and other objectives are fulfilled by the present invention which concerns a unique class of chiral compounds that can be used alone as the optically-active additive or dopant in nematic liquid crystals to achieve a reflective wavelength that is temperature independent or essentially temperature independent, i.e., a $d\lambda/dT$ approaching zero in value, yet without significantly reducing the temperature range of the liquid crystalline phase, or diluting or otherwise adversely affecting its needed physical properties for liquid crystal implementations.

The inventive compounds are derivatives of dioxolanes and have the molecular structure generally indicated in Fig. 1 and reproduced below as general formula I.

I



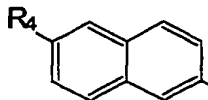
The R , R_1 , R_2 and R_3 substitutions on the molecule of general formula I control the temperature dependence of the twisting power in the nematic host mixture in a surprisingly superior fashion. Generally, the R_2 and R_3 groups at the number 2 position of the dioxolane

ring independently are hydrogen, methyl or another lower alkyl group, or a substituted aryl or biaryl unit, while the R_1 groups independently each are a hydroxyl, alkoxy, aryloxy, or arylalkoxy group. The R groups in general formula I indicate a group of general formula II, which is as follows:



where A_1 is an aromatic group, an acyclic aliphatic group, or an alicyclic group (e.g., a mono- or polycyclic aryl group, a straight chain or branched chain alkyl group, an arylalkyl group, an arylalkenyl group, a cycloalkyl group, a cycloalkenyl group), and A_1 can be a substituted or unsubstituted group. For example, A_1 can be benzyl, cinnamyl, phenethyl, cyclohexyl, and the like. Z is a group selected from -O-, -OCO-, or -S-, and the coefficient q is 0 or 1. Z can also be $(CH_2)_nO$ with the coefficient n being 0 to 5 and the coefficient q being 1. A_2 is a bivalent radical of naphthalene that may additionally be substituted. Preferably, A_2 is a bivalent radical (2,6- or 1,5-disubstituted) of naphthalene, which may be unsubstituted or substituted (e.g., methyl, cyano, halogeno, amino, nitro, or hydroxyl substituents). The ring structure of A_2 , or A_1 if it is cyclic, optionally can be heterocyclic, such as by replacement of one or more CH member(s) of the ring structure with N, O and/or S (e.g., a bivalent radical of quinoline, xanthene, carbazole, or acridine).

In one preferred embodiment, each R substituent of general formula I is independently selected as:



where R_4 can be represented by general formula III as follows:



BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is the general chemical structure of the dioxolane derivatives according to the present invention, where the R_1 , R_2 , R_3 , and R_4 substituents control the temperature dependence of the twisting power in a superior manner.

5

Fig. 2 is the chemical structure of a preferred inventive compound embodied by the formula of Fig. 1, viz., (4R,5R)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis[6-(benzyloxy)naphth-2-yl]-1,3-dioxolane-4,5-dimethanol, which has been experimentally demonstrated to provide low $d\lambda/dT$ in certain nematic host mixtures.

10

Fig. 3 is a graph showing the peak reflection wavelength (nm) versus temperature results for experimental tests performed with respect to a variation in color for two compounds in the E44 nematic host mixture. A substitution on the naphthalene units shows a dramatic change in the $d\lambda/dT$ results.

15

Fig. 4 is a graph showing the peak reflection wavelength (nm) versus temperature results for experimental tests performed on the dimethanoldioxolane compound from Fig. 2 in E44 nematic host mixture tested with and without UCN additive.

20

DETAILED DESCRIPTION OF THE INVENTION

In this invention, a new class of derivatives of dioxolanes embodied by the formula of Fig. 1 has been discovered that provide a substantially temperature independent dp/dT over a wide operating temperature range when added to nematic liquid crystalline mixtures with physical properties that are useful in cholesteric displays, including commercially viable cholesteric displays. The inventive chiral compounds are especially useful as additives to nematic liquid crystals for use in cholesteric displays to achieve needed properties for their practical use, particularly in portable device applications. Significantly, this invention provides this utility while only requiring the use of a single type of chiral additive compound within the scope of the invention, as described herein, and without requiring a mixture of different types of chiral additives.

30

where n is an integer value of 0 or 1 or more, X is $-\text{CH}=\text{CH}-\text{CH}_2-$, or $-(\text{CH}_2)_m-$ where m is an integer value of 1, 2, 3, or more. Y is a radical of an aromatic hydrocarbon, an acyclic aliphatic hydrocarbon, or an alicyclic hydrocarbon group (e.g., a mono- or polycyclic aryl group, a straight chain or branched chain alkyl group, a cycloalkyl group, a cycloalkenyl group, and the like), and Y can be a substituted or unsubstituted group. Z and q have the same
5 respective meanings as defined above relative to general formula II.

In one preferred embodiment, R_4 is an aryloxy, an arylalkoxy, an arylalkyleneoxy, or an arylalkenyleneoxy group. Examples of R_4 advantageously may include, for instance,
10 benzyloxy ($\text{C}_6\text{H}_5-\text{CH}_2-\text{O}-$), cinnamyloxy ($\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CH}_2-\text{O}-$), phenethyloxy ($\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\text{O}-$), and the like, where R_1 is a hydroxy group and R_2 and R_3 are methyl groups.

Additionally, the specific structures of the four R groups present in formula I or Fig. 1 can be identical to each other or they can independently vary from each other within the
15 guidelines indicated above and herein.

The inventive optically-active, chiral additives according to the formula of Fig. 1 contain a sufficiently high helical twisting power (HTP) so that only a relatively small amount of the chiral additive is required to twist the nematic phase to a pitch length where it
20 reflects wavelengths in the visible or infrared portion of the electromagnetic spectrum. On the other hand, the HTP of the additive is not inordinately high either, so that the invention can avoid undesired gradients in concentration, which could cause undesired inhomogeneities in the display. The present invention thereby avoids the need to combine separate types of chiral compounds in order to achieve a very high degree of temperature independence. While the
25 present invention does not necessarily exclude the possibility, and in fact does contemplate, use of mixtures of different inventive chiral compounds within the scope of the formula of Fig. 1, the important point is that the inventive chiral compounds can be effectively used singly in a liquid-crystalline nematic mixture deployed in a light modulating apparatus to avoid the need for chiral additive combinations.

Commercially viable displays require a liquid crystal mixture that has a dielectric anisotropy, birefringence and desired elastic and viscosity coefficients to provide a display with suitable brightness, contrast, and speed. The dielectric anisotropy and viscosity must be such that low voltage pulses can be used to reduce the cost of the electronic drive chips as well as implement drive schemes and waveforms for rapidly addressing the display. The birefringence has to be large to provide high brightness. Furthermore, the materials must not provide undesirable features to the display such as image sticking or phase separation. Cholesteric displays therefore require very special cholesteric materials. Cholesteric displays incorporating the inventive dioxolane derivatives satisfactorily meet all these criteria and requirements, while providing superior temperature independence performance and so forth.

Namely, the invention provides chiral compound additives to nematic liquid crystals that provide at least the following features important for cholesteric displays:

1. Solubility in nematic liquid crystals that have the physical properties necessary for cholesteric displays.
2. Possess a helical twist power (HTP) generally ranging from $15\ \mu\text{m}^{-1}$ to $200\ \mu\text{m}^{-1}$, and more usually from $30\ \mu\text{m}^{-1}$ to $90\ \mu\text{m}^{-1}$. HTP values in this range are not so small as to dilute the important physical properties of nematic liquid crystals when twisted to reflect light in the visible spectrum. In addition, these values are not so large that slight inhomogeneities in the mixture caused by phase separation can disfigure the display.
3. Provide a substantially temperature independent HTP in the cholesteric phase over the operating temperature range of cholesteric displays of commercial value.
4. Do not decompose under ultraviolet light of exposures under common environmental conditions.
5. Do not chemically react with the host nematic liquid crystal.
6. Possess the property that the temperature dependence can be modified by the addition of an achiral additive to the nematic liquid crystal. Such an additive may or may not possess a liquid crystalline phase.

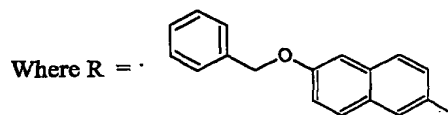
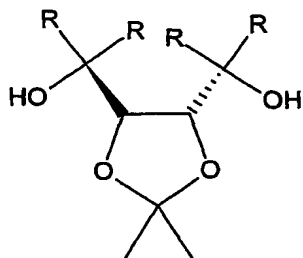
As compared to the competing contemporarily available chiral additives that have twisting powers typically of $\beta < 15\mu\text{m}^{-1}$ when X is measured in weight percent, the new soluble chiral additive materials, invented here, have values of β approaching $80\mu\text{m}^{-1}$. This is a substantial improvement since the concentration of the chiral additive in this invention can be so small as to have a near negligible effect on the physical properties of the nematic liquid crystal.

Chiral nematic liquid crystalline materials within the scope of this invention, which include an inventive chiral additive and a nematic host mixture, can be implemented in cholesteric liquid crystal displays, electro-optical cells, and light modulating apparatuses in manners, arrangements and/or systems consistent with the descriptions, such as set forth in U.S. Patent Nos. 5,251,048, 5,384,067, 5,437,811, and 5,453,863, whose descriptions are incorporated by reference.

EXAMPLES

Synthesis Scheme for Chiral Additive:

One illustrative inventive compound, (4R,5R)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis[6-(benzyloxy)naphth-2-yl]-1,3-dioxolane-4,5-dimethanol, is shown in Fig. 2 and is reproduced below. The dimethanoldioxolane has 2,6-substituted naphthalene units.



The inventive compound of Fig. 2 was synthesized according to the following protocol with reference to the reaction Scheme I provided below.

Synthesis of 2-(Benzyloxy)-6-bromonaphthalene (2) intermediate:

A mechanically stirred mixture of 6-bromonaphth-2-ol (10.00g, 0.04483mol), benzyl bromide (6.97g, 0.0408mol), potassium carbonate (11.26g, 0.08147mol) and butan-2-one

(350ml) was heated under reflux for 24 hrs. (GLC and TLC analyses revealed a complete reaction). The potassium carbonate was filtered off and the filtrate was washed with water before being dried (MgSO₄). The drying agent was filtered off and the solvent was removed *in vacuo* to give a pale orange solid. The crude product was crystallized twice from ethanol and was dried *in vacuo* (P₂O₅, CaCl₂, paraffin wax, 48h) to afford white crystals. Yield = 11.97g (94%), mp 113-114°C.

Synthesis of product compound - compound (4):

(4R,5R)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis[6-(benzyloxy)naphth-2-yl]-1,3-dioxolan-4,5-dimethanol (4):

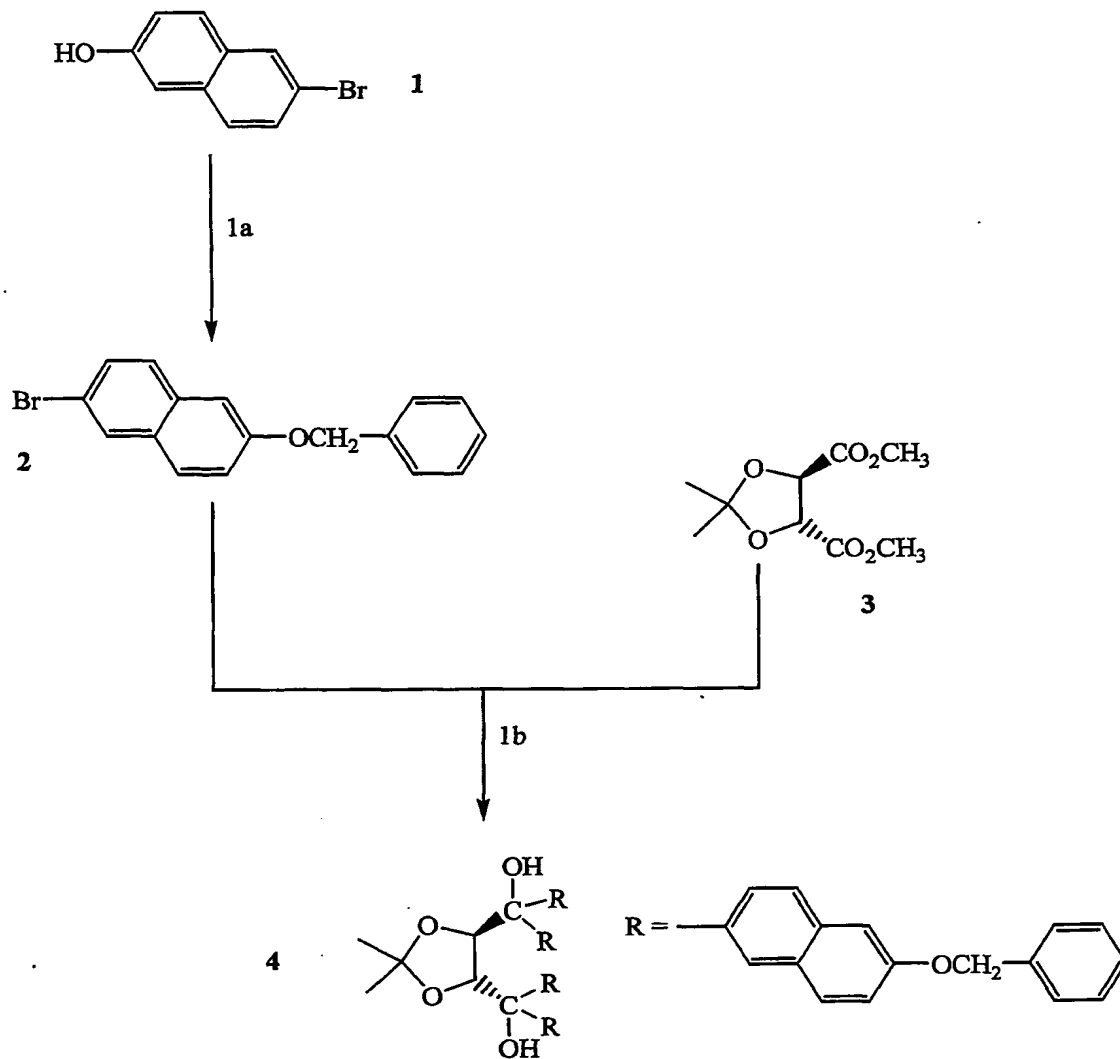
n-Butyllithium (5.37ml, 2.5M in hexane, 0.0134mol) was added dropwise at -74°C to -77°C to a mechanically stirred, cooled (-77°C) solution of compound 2 (4.20g, 0.0134mol) in dry tetrahydrofuran (350ml) under dry argon. Once the addition was complete, the reaction mixture was maintained under these conditions for a further 2 hrs. (GLC analysis revealed a complete reaction) before the reaction mixture was allowed to warm to -25°C.

2,3-O-Isopropylidene-L-tartrate (0.73g, 0.03345mol) was added to the reaction mixture at -20°C to -25°C (exothermic) and the reaction mixture was allowed to warm to room temperature. The reaction mixture was stirred at room temperature for a further 15 hrs. before saturated ammonium chloride (60ml) was added and the mixture stirred for a further 4 hrs. The reaction mixture was washed with diethyl ether (3 x 75ml) and the combined organic washings were dried (MgSO₄). The drying agent was filtered off and the solvent was removed *in vacuo* to give an orange semi-solid.

The crude product was purified twice by column chromatography [silica gel / hexane, ethyl acetate, 4:1] followed by further chromatography [silica gel / hexane, diethyl ether, 4:1]. The product was crystallized from toluene to afford a pale yellow solid, which was dried *in vacuo* (P₂O₅, CaCl₂, paraffin wax, 48h).

Yield = 7.30g (50%).

Scheme 1



1a...Benzyl bromide, K_2CO_3 .
1b...(i) n-Butyllithium; (ii) NH_4Cl .

Example 1:

Experimental studies were performed on the dimethanoldioxolane compound (4) described above and of the structure shown in Fig. 2, and separately on (4R,5R)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis[naphth-2-yl]-1,3-dioxolane-4,5-dimethanol as a comparative compound, each in a E44 nematic host mixture, the results of which were plotted in Fig. 3 as a graph showing the peak reflection wavelength (nm) versus temperature. The respective cholesteric liquid crystal mixtures prepared for conducting these experimental studies were as follows.

COMPOSITION 1 formulation:

<u>Component</u>	<u>Component amt. (wt%)</u>
2-naphthyl as the R groups on the dimethanoldioxolane (comparative compound)	3.4%
E44	96.6%

COMPOSITION 2 formulation:

<u>Component</u>	<u>Component amt. (wt%)</u>
6-benzyloxynaphth-2-yl as the R groups on the dimethanoldioxolane (compound (4), Fig. 2 compound)	10.0%
E44	90.0%

It will be noted that E44 is commercially available nematic liquid crystal mixture that was obtained from Merck KgaA in Darmstadt, Germany through EM Industries in Hawthorne, New York. It will also be noted that the percentage of compound (4), and thus the percentage of E44, advantageously can be varied to achieve the desired reflective wavelength. For example, varying the percentage of compound (4) from 10 wt% to 2 wt% changes the reflective wavelength from the visible into the infrared. Finally, it will be noted that other additive materials can be included in the cell material to improve other cell properties.

As to the cholesteric display test cell arrangement used, both mixtures, i.e., Compositions 1 and 2, were vacuum filled in separate surface stabilized cholesteric displays with a 5 μ m cell spacing. To accomplish this, two glass plate substrates were put together using an epoxy material around the perimeters with the substrates separated by 5 micron spacers and a small hole left in the perimeter seal for introducing the liquid crystal. The inner
5 faces of the glass substrates were coated with indium-tin oxide (ITO), a standard insulating layer, and a polyimide layer for liquid crystal alignment. The back plate was painted black. The liquid crystal mixture was vacuum filled into the provided cell so that each liquid crystal mixture was sandwiched between the two glass plate substrates.

The arrangement used to control the temperature of the liquid crystal mixtures samples being tested was as follows. A liquid nitrogen cryostat was used to control temperature on the test cells. The cryostat had a cold finger and a heater. The cryostat system was obtained from Janis Cryogenics. A white light source was used with a monochromator,
15 both obtained from Oriel. A silicon detector was used to detect the light intensity. To measure the color, the cell was switched to the reflecting planar state at each temperature and the peak reflection wavelength was determined. The peak reflection wavelength of the cells was measured with incident light at the surface normal and reflected light detected at 45°. The switching pulse used had a magnitude (amplitude and width) high enough to transform the
20 texture to the reflecting planar texture at each temperature. The pulse was an AC square pulse. Data points were typically acquired every 10°C from -20°C to about +70°C. The results of these measurements are plotted in Fig. 3.

The compound of Fig. 2 was found through these experimental studies to possess a
25 substantially temperature independent HTP in the nematic mixture E44, which is suitable for cholesteric displays. The HTP for this compound at room temperature in E44 is 31 μ m⁻¹. The HTP for the base compound (unsubstituted naphthalene units) is 91 μ m⁻¹. A plot of the temperature dependence of the compound according to the present invention, a compound containing (4R,5R)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis[6-(benzyloxy)naphth-2-yl]-1,3-dioxolan-
30 4,5-dimethanol, versus that of the comparative reference compound, i.e., a similar compound containing a small amount by weight of (4R,5R)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis[naphth-2-yl]-

1,3-dioxolane-4,5-dimethanol, which is strongly temperature dependent, is shown in Fig. 3. It should be noted that both molecules exhibit a linear temperature dependence from -20°C to +70°C.

5 In addition to the use of a single chiral additive, independence of the helical twisting power with temperature advantageously can be obtained by mixing two dioxolane materials that are structurally different and that exhibit opposite twist senses.

Example 2:

10 ADDITIONAL STUDIES INVOLVING ACHIRAL COMPOUND ADDITIVE:

The change in color of a liquid crystal mixture containing a chiral compound (viz., compound 4, Fig. 2 compound) and a host mixture (viz. E44) along with a small amount of an achiral non-liquid crystalline compound (undecyl cyanide at 4% by weight) was investigated. The components were mixed according to the following proportions as

15 Composition 3:

COMPOSITION 3 formulation:

<u>Component</u>	<u>Component amt. (wt%)</u>
6-benzyloxynaphth-2-yl as the R groups on the	11.0%
20 dimethanoldioxolane (compound (4), Fig. 2 compound)	
E44	85.0%
UCN (undecyl cyanide, C ₁₁ H ₂₃ CN)	4.0%

25 The resulting liquid-crystalline mixture containing the achiral additive was filled into a cell and tested using the arrangement described in Example 1. The results of these additional experiments investigating the possible effect of certain achiral additives to the liquid crystalline nematic mixture are shown in Fig. 4, and the plot of the results obtained for Composition 2 in Example 1 as indicated in Fig. 3 was included for sake of comparison. The inventive chiral dimethanoldioxolane compound used for these studies was used to twist the
30 nematic phase to a blue reflecting pitch length. Referring to Fig. 4, a subtle difference between the two curves was clearly evident. Without the achiral additive, the $d\lambda/dT$ is nearly

flat with a slightly negative value, whereas with the achiral additive, the $d\lambda/dT$ is nearly flat with a slightly positive value. The helical twisting power for the dimethanoldioxolane compound is similar for the two nematic mixtures in Fig. 4 with the additive host mixture showing a slightly higher HTP.

5

It should be noted that UCN is representative of a class of achiral compounds of the general structure R^1CN where $R^1 = \text{alkyl}$. $R^1 = C_{11}H_{23}$ - for UCN itself.

Thus, a further discovery of this invention is that fine-tuning can therefore be performed using certain achiral non-liquid crystalline compounds added to a cholesteric system with a nematic host mixture and a single chiral compound.

For practicing this further embodiment, the achiral additive, namely, aliphatic nitriles, can be commercially obtained from Aldrich Chemicals or prepared by conventionally known methods. Useful alkyl nitriles as the achiral additive include 5C-17C alkanenitriles, and more preferably 8C-14C straight chain or n-alkane nitriles. One preferred alkyl nitrile is undecanenitrile, using IUPAC nomenclature (alternatively, referred to as undecyl cyanide, in common nomenclature). These achiral additives have been found to be effective in amounts of approximately 2 to 6 wt% of the overall liquid-crystalline mixture.

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Although E44 was exemplified above, virtually any nematic host mixture, including cyanobiphenyls known in the art, can be used in the practice of this invention. The inventive chiral compounds are readily soluble, as required, in many commercially available nematic host mixtures.

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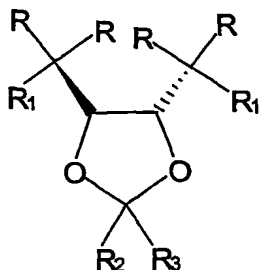
While this invention has been described in terms of its preferred embodiments, those skilled in the art will recognize that the invention can be practiced with modification within the spirit and scope of the appended claims.

APPENDIX: References Cited

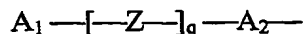
1. U.S. Patent No. 5,251,048: "Method and Apparatus of Electronic Switching of a Reflective Color Display", J. W. Doane, D.-K. Yang, October 1993.
2. U.S. Patent No. 5,384,067: "Grey Scale Liquid Crystal Material", J. W. Doane, D.-K. Yang, January 1995.
3. U.S. Patent No. 5,437,811: "Liquid Crystalline Light Modulating Device and Material", J. W. Doane, D.-K. Yang, L.-C. Chien, August 1995.
4. U.S. Patent No. 5,453,863: "Multistable Chiral Nematic Displays", J. West, D.-K. Yang, September 1995.
5. "Cholesteric Structure – II: Chemical Significance", p105 – 119, J. L. Fergason, N. N. Goldberg, R. J. Nadalin, *Liquid Crystals*, Ed. G. H. Brown, G. J. Dienes, M. M. Labes, Gordon and Breach Science Publishers, New York (1966)
6. "Induced Cholesteric Mesophases: Origin and Application, G. Gottarelli, G. P. Spada, *Mol. Cryst. Liq. Cryst.*, 123, 377 – 388 (1985)
7. U.S. Patent No. 5,309,265: "Short Pitch LC layer with a temperature Independent λ_0 and Containing a Nematic LC Doped with Plural Chiral Additives Having the Same Twist Sense", R. Buchecker, J. Funfschilling, M. Schadt, May 1994.
8. "TADDOLs with Unprecedented Helical Twisting Power in Liquid Crystals", H.-G. Kuball, B. Weiss, A. K. Beck, D. Seebach, *Helvetica Chimica Acta*, 80, 2507-2514 (1997)
9. "TADDOLs Under Closer Scrutiny – Why Bulky Substituents Make it All Different", A. K. Beck, M. Dobbler, D. A. Plattner, *Helvetica Chimica Acta*, 80, 2073-2083 (1997)
10. U.S. Patent No. 5,637,255: "Chiral Dioxolanes", S. Kelly, M. Schadt, June 1997.

WHAT IS CLAIMED IS:

1. An optically active compound of the formula:

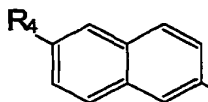


where the R_2 and R_3 groups are methyl, another lower alkyl group or an aryl or biaryl unit while the R_1 groups independently each are a hydroxyl, alkoxyl, aryloxy, or arylalkoxy group, the R groups each represent a group as follows:

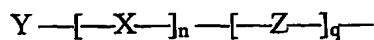


where A_1 is an aromatic group, an acyclic aliphatic group, or an alicyclic group, and A_1 can be a substituted or unsubstituted group, Z is a group selected from $-O-$, $-OCO-$, or $-S-$, and the coefficient q is 0 or 1. Z may also be $(CH_2)_nO$ where the coefficient n is 0 to 5 and the coefficient q is 1. A_2 is a bivalent radical of a naphthalene group, and the cyclic structure of A_2 , or A_1 if it is cyclic, optionally can be heterocyclic, such as by replacement of one or more CH member(s) of the ring structure with N, O and/or S.

2. The optically active compound of claim 1, where each R substituent is independently selected as:



where R_4 represents a group as follows:



where n is an integer value of 0 or 1 or more, X is $-\text{CH}=\text{CH}-\text{CH}_2-$, or $-(\text{CH}_2)_m-$ where m is an integer value of 1, 2, 3, or more, Y is a radical of an aromatic hydrocarbon, an acyclic aliphatic hydrocarbon, or an alicyclic hydrocarbon, and Y can be a substituted or unsubstituted group, and Z and q have the same respective meanings as defined in claim 1.

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3. The optically active compound of claim 2, where R_4 is an aryloxy radical, an arylalkoxy radical, an arylalkyleneoxy, or an arylalkenyleneoxy radical.

4. (4R,5R)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis[6-(benzyloxy)naphth-2-yl]-1,3-dioxolane-4,5-dimethanol.

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5. A liquid crystalline mixture, comprising:

a liquid-crystalline base having liquid crystalline properties;

at least one optically active compound of the formula as described in

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any of one of claims 1-4.

6. The liquid crystalline mixture according to claim 5, further including an achiral non-liquid crystalline compound.

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7. The liquid crystalline mixture according to claim 6, wherein the achiral non-liquid crystalline compound comprises $R^1-\text{C}\equiv\text{N}$, where R^1 represents an aliphatic group.

8. The liquid crystalline mixture according to claim 7, wherein $R^1-\text{C}\equiv\text{N}$ comprises an alkynitrile.

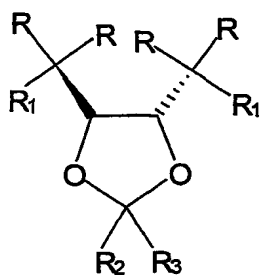
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9. The liquid crystalline mixture according to claim 7, wherein $R^1-\text{C}\equiv\text{N}$ comprises undecanenitrile.

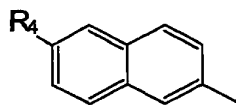
10. An electro-optical cell comprising a layer including a liquid crystalline mixture as described in any one of claims 5-9 sandwiched between two substrate means, and means for applying an electric potential to the substrate means.

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5 FIG. 1



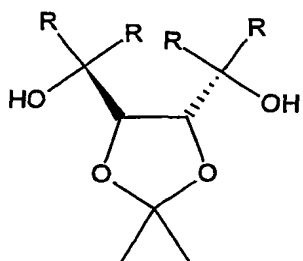
Where R =



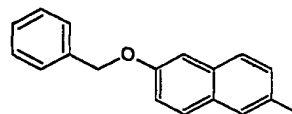
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FIG. 2

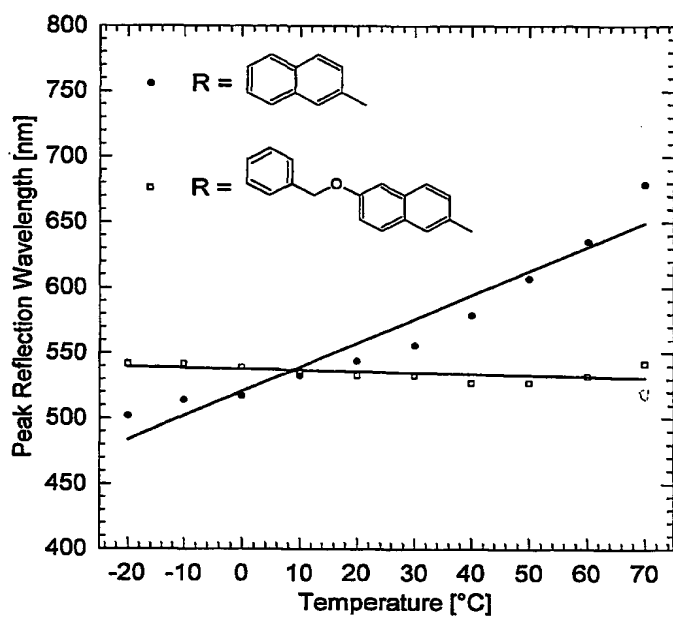


Where R =



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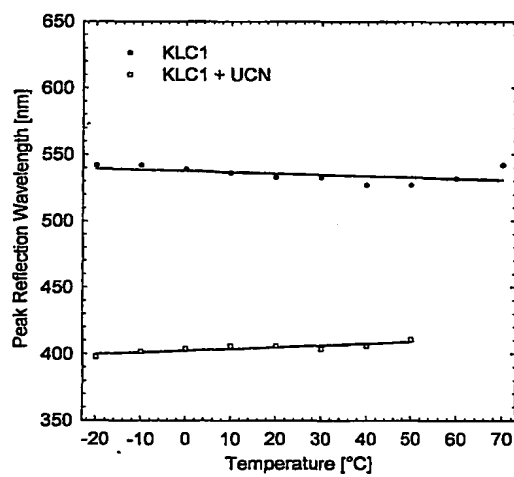
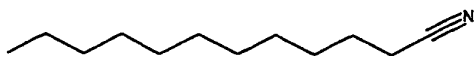
FIG. 3



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FIG 4

where UCN is undecyl cyanide:



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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/14842

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C09K 19/34, 19/32, 19/36; C07D 317/12

US CL : 252/299.01, 299.61, 299.62, 299.7; 428/1.1, 549/430, 453

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/299.01, 299.61, 299.62, 299.7; 428/1.1, 549/430, 453

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST 2.0, CAS online

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Kuball et al., "TADDOLs with Unprecedented Helical Twisting Power in Liquid Crystals", Helv. Chim. ACTA, Vol. 80, pages 2507-2514, 1997, see whole document	1, 5-6
Y		10-17
X	Chem. abstr., Vol. 124, No. 1996 (Columbus, OH, USA), page 9072, the abstract No. 9076r, Quinkert, Gerhard et al., " Total Synthesis with a Chirogenic Opening Move Demonstrated on Steroids with Estrane or 18-homoestrane Skeleton". Helv. Chim. Acta 1995, 78(5), 1345-91 (Eng). see RN 170709-36-1.	1, 5

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"G" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

24 AUGUST 2001

Date of mailing of the international search report

11 OCT 2001

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